

Polarization Saturation in Strained Ferroelectrics

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Abstract

Using density-functional calculations we study the structure and polarization response of tetragonal PbTiO_3 , BaTiO_3 and SrTiO_3 in a strain regime that is previously overlooked. Different from common expectations, we find that the polarizations in all three substances saturate at large strains, demonstrating a universal phenomenon. The saturation is shown to originate from an unusual and strong electron-ion correlation that leads to cancellation between electronic and ionic polarizations. Our results shed new insight on the polarization properties, and reveal the existence of a fundamental limit to the strain-induced polarization enhancement.

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Response of electrical polarization to external strains in infinite solids is a subject of interest from both fundamental and technological points of view.[1] Fundamentally, the process is governed by electrons, ions and their complex interactions, forming an important class of collective phenomena. Seeking direct physics and/or mechanism underlying the responses is of key relevance. Previously, Ederer and Spaldin showed that the strain dependence of polarization in different substances (BaTiO_3 , BiFeO_3 , LiNbO_3 , and PbTiO_3) could be understood by the piezoelectric and elastic constants of the *unstrained* materials.[2] Technologically, inplane compressive strains were able to dramatically raise the critical transition temperature in BaTiO_3 (Ref.3) and to turn incipient SrTiO_3 into strongly ferroelectric [4]. These important studies focus on small strains near equilibrium.

Nowadays, advance in experimental fabrication of various high-quality ferroelectric(FE) nanostructures[5] (such as thin films, nanowires, and dots) opens an opportunity for studying polarization response in a new regime with medium and/or large strains that have not been previously investigated [2, 3, 4]. Unlike bulks, FE wires or dots allow exceedingly large external strains without formation of dislocation, since stress can be effectively relaxed due to finite lateral size.[6] For instance, large compressive strains can be realized in FE nanorods[7] by compressing them along the lateral directions. Even for thin films, strains of more than 3% were shown possible in $\text{LaAlO}_3/\text{SrTiO}_3$. [8] The new strain regime is interesting and may reveal many new physics in the sense that the charge density is *heavily* deformed by large strains, making electrons behave more collectively in some spatial region, but less in another. As a result, answers to questions (1) what determine FE off-center displacements in the new strain regime, and (2) how piezoelectric response, as a collective phenomenon, adjusts itself to large strains, remain unknown and are important. Furthermore, based on the widely accepted conclusion that polarization is to be enhanced as compressive strain increases[2, 3, 4], scientists have been long wondering what is the upper limit that polarization is able to reach, provided that exceeding strain is possible in laboratory.[9] This is an intriguing question since it defines a profound limit on our widespread effort of seeking enhanced polarization by strain.[3, 4]

Here by means of first-principle calculations we investigate the structure and polarization responses of FE perovskites in the new strain regime. Three paradigm materials [namely, PbTiO_3 (PT), BaTiO_3 (BT), and SrTiO_3 (ST)] are studied, aimed to obtain conclusions that are generally applicable. We find that polarizations in considered FEs show a universal

behavior, by exhibiting three distinct stages in their strain-induced responses (each stage producing dissimilar piezoelectric coefficients). Two out of these three stages are new and previously unknown. We further reveal that when the compressive inplane strain is high, the polarization will no longer increase, defying the common belief that polarization must increase with increasing compressive strain. In fact, our calculations predict the existence of a critical inplane strain, above which the polarization starts to saturate. Our results suggest that there is a fundamental constraint on polarization enhancement by mechanical strain.

Three considered materials represent FEs of different magnitudes of polarization: PbTiO_3 is strongly ferroelectric, BaTiO_3 is ferroelectric but with a weaker polarization, and SrTiO_3 is not FE under zero strain. We study the structural phase of tetragonal symmetry ($|\mathbf{a}_1|=|\mathbf{a}_2|=a$, $|\mathbf{a}_3|=c$), in which materials can have polarizations along the $[001]$ direction. Biaxial in-plane strain (in Voigt notation) is defined as $\eta_1=\eta_2=(a-a_0)/a_0$, where a_0 is the unstrained in-plane lattice constant.

Polarization in infinite periodic solids can be expressed in lattice-vector coordinate as $\mathbf{P} = \frac{e}{\Omega}(\chi_1\mathbf{a}_1 + \chi_2\mathbf{a}_2 + \chi_3\mathbf{a}_3)$, where Ω is the volume of a unit cell and χ_i describes the polarization along the direction of lattice vector \mathbf{a}_i . Displacement of ions and deformation of electron density both contribute to \mathbf{P} . Computing of ionic contribution (labeled as \mathbf{P}_{ion}) is straightforward using point charges, while electronic contribution (denoted as \mathbf{P}_{el}) is determined using the modern theory of polarization[10, 11], as implemented in our mixed-basis method. More specifically, \mathbf{P}_{el} is computed as the geometrical Berry phase of valence electron states as $\mathbf{P}_{\text{el}} = i\frac{2e}{(2\pi)^3} \int d\mathbf{k}_1 \nabla_{\mathbf{k}_2} \phi(\mathbf{k}_1, \mathbf{k}_2)|_{\mathbf{k}_1=\mathbf{k}_2}$, where $\phi(\mathbf{k}_1, \mathbf{k}_2) = \ln \det | \langle u_{m\mathbf{k}_1} | u_{n\mathbf{k}_2} \rangle |$ is the phase of the determinant formed by occupied Bloch wave functions $u_{n\mathbf{k}}$. When inplane strains are imposed, two factors give rise to the change in polarization: (1) the variation of χ_i , and (2) the cell-structure modifications of Ω and \mathbf{a}_i . The first factor is critical and is manifested[12, 13] in the *proper* piezoelectric coefficients as $e_{\alpha\beta\gamma}^{\text{pro}} = \frac{e}{\Omega} \sum_i \frac{d\chi_i}{d\epsilon_{\beta\gamma}} a_{i\alpha}$, where $\epsilon_{\beta\gamma}$ is the strain in Cartesian notation. The second factor contributes to the improper piezoelectric coefficient which is trivially related to the proper one by the magnitude of polarization as $e_{\alpha\beta\gamma}^{\text{impro}} = e_{\alpha\beta\gamma}^{\text{pro}} + \delta_{\alpha\beta} P_\gamma - \delta_{\beta\gamma} P_\alpha$. One thus notes that χ_i is a critical quantity that is technologically relevant in terms of obtaining high piezoelectric efficiency. This study will be concerned with the strain dependence of χ_i .

Technically, we use density functional theory within the local density approximation (LDA)[14] to determine optimized cell shape and atomic positions by minimizing the total

energy. Calculations are performed using pseudopotential method with mixed-basis set.[15] The Troullier-Martins type of pseudopotentials are used[16]; atomic configurations for generating pseudopotentials, pseudo/all-electron matching radii, and accuracy checking were described elsewhere.[17] For each in-plane strain, the out-of-plane c lattice constant and atomic positions are fully relaxed. Our LDA-calculated inplane lattice constants of unstrained bulks are $a=3.88\text{\AA}$ for PT, $a=3.95\text{\AA}$ for BT, and $a=3.86\text{\AA}$ for ST, which all agree well with other existing calculations.

Structural response: Fig.1(a) depicts the c/a ratios of the three considered materials under compressive strains. Let us examine the BaTiO₃ curve first. For this curve, (1) our calculations confirm the (expected) linear relation between c/a and a when inplane strain is small; (2) However, as the inplane a length is decreased to 3.82\AA [point A in Fig.1(a)], BaTiO₃ apparently enters a different state, as witnessed by the fact that the c/a rises more sharply afterwards; (3) Interestingly, when a reaches point B, the c/a becomes linear again. These results combine to make the c/a in the region between A and B appear to be notably enhanced. This enhanced c/a regime in FEs has not been emphasized before (since previous studies deal with small strains)—and provides an explanation for the (mysterious) enlarged electromechanical response recently observed in PZT films under very large electric fields[18], because these fields drive the films into the new strain range between A and B.

Contrast of three materials in Fig.1(a) tells us that the above conclusions are applicable also for PbTiO₃ and SrTiO₃. But the c/a value and the location of point A reveal interesting differences. First, we predict that for a fixed a constant, BaTiO₃ exhibits a *larger* c/a than PbTiO₃, unlike the zero-strain case where PT has a much higher c/a ratio of ~ 1.04 (in LDA). Meanwhile, the c/a in SrTiO₃ is considerably lower than in BT or PT, which could be attributed to the small size of Sr. When strained, the big Ba and Pb atoms repel other atoms more forcefully, leading to large c lengths. This size difference is also reflected in the location of the critical A point (at which the c/a changes behavior). The a value of point A is remarkably similar for PT and BT, but not for ST.

Fig.1(b) shows atomic off-center displacements (in unit of c) in BaTiO₃ under different strains, obtained by placing the Ba atom at the cell origin and then determining the displacements of Ti, O1 and O2 atoms with respect to their high-symmetry locations in tetragonal structure. Labels of individual atoms are given in the inset of Fig.1(b). Atomic displacements in Fig.1(b) explain why point A plays an important role in determining the

structural response. When $a > a_A$ (lower strains), the O displacements are small. But, as a is below a_A , the oxygen off-center shifts increase dramatically with a markedly different slope. Furthermore, the Ti displacement is positive (out of phase with the O displacement) when $a > a_A$, and then becomes negative (in phase with the O displacement) for $a < a_A$.

Given the complexity in atomic displacements as well as in the c/a ratio, one would desire to find a mechanism (if any) that may determine how, and in what magnitudes, atoms are displaced. For this purpose, we examine the bond lengths in strained BaTiO₃, shown in Fig.1(c). Two observations are ready: (1) The Ti-O1 distance correlates well with the c length, (2) Despite that a is significantly compressed [by $\sim 0.5\text{\AA}$ in Fig.1(a)], the Ti-O2 and Ti-O3 distances remarkably maintain to be nearly constant (so are the Ba-O1 and Ba-O2 bondlengths). Our calculations thus reveal the existence of a simple (and preferred) rule that can quantitatively explain the structural response *over a wide range* of inplane strains, that is, FEs respond to the external strains in a manner that maintains the lengths of short Ti-O and Ba-O bonds. This rule is found true also for PT and ST, and may be easily verified in x-ray experiments.

Nevertheless, FE perovskites do not maintain the bond lengths in a trivial way. In Fig.1(d) we describe the strain dependence of the optimal cell volume. Though cell volume is often assumed to be constant under biaxial strains, obviously this is not the case for FEs. Instead, Fig.1(d) displays features that are very suggestive in terms of understanding the structure and polarization responses. Under small strains, the cell volume first decreases. This decrease is most pronounced in SrTiO₃. Then approximately at a_A , the volume of the material increases quickly, and later at a_B , it starts to decrease again. One thus sees that between a_A and a_B the enhanced c/a in Fig.1(a)—and the enlarged O displacements in Fig.1(b)—occur by *the expansion of cell volume*.

Polarization response: Fig.2(a) depicts the χ_3 polarization and the proper e_{31}^{pro} piezoelectric coefficient in PbTiO₃ under varied compressive strain. Caution is made to ensure that we follow continuously the same polarization as the χ_3 crosses different branches, since polarization in periodic solids is a multi-valued quantity. At zero strain, PbTiO₃ shows a theoretical χ_3 of 0.63 that corresponds to a polarization of $66.7\mu\text{C}/\text{cm}^2$, consistent with the experimental result[19] of $\sim 70\mu\text{C}/\text{cm}^2$. Upon strain, the most notable result in Fig.2(a) is that PbTiO₃ displays three stages (labeled as I, II, and III) in its polarization response.

At stage I (when a is above 3.84\AA), the χ_3 polarization increases linearly, from which

the piezoelectric e_{31}^{pro} coefficient is deduced as $637 \mu\text{C}/\text{cm}^2$. At stage II, the $\chi_3 \sim a$ relation remains linear, but shows a different slope from that of stage I. We numerically find that the e_{31}^{pro} for stage II is $898 \mu\text{C}/\text{cm}^2$. Interestingly, when the inplane strain continuously transitions from stage I to II, we notice an abrupt rise in the polarization. This leads to the occurrence of a huge piezoelectric e_{31}^{pro} coefficient of $3900 \mu\text{C}/\text{cm}^2$ near $a = 3.84\text{\AA}$.

When the inplane a constant is further decreased below 3.70\AA (which corresponds to a moderate 4.5% strain), another unusual phenomenon occurs in Fig.2(a). That is, the increase in polarization dramatically slows down, and the χ_3 finally *saturates* at a value of 1.05. Further increase of inplane strain no longer affects the χ_3 polarization. This saturation is surprising, since it is generally accepted that FE polarization always increases with increasing compressive strains. The saturated polarization also demonstrates the existence of a maximal limit up to which polarization can be enhanced by means of epitaxial strains.

We have also performed polarization calculations for BaTiO_3 and SrTiO_3 ; results are shown in Fig.2(b). For incipient SrTiO_3 , we find a threshold strain at $\eta_1=1\%$, below which the polarization remains null. A similar magnitude of threshold strain was reported previously.[20] Results for BaTiO_3 and SrTiO_3 in Fig.2(b) reveal that (1) the existence of a three-stage polarization response and (2) the saturation of polarization apply to all three substances, hence demonstrating a general phenomenon. Also interestingly, we find that χ_3 saturates at similar values in BaTiO_3 and in SrTiO_3 , but differently in PbTiO_3 .

The saturation of χ_3 can not be naively related to the saturations of effective charges and/or atomic displacements. First, we see in Fig.1(b) that the O displacements do not saturate, in fact. To illustrate if effective charge saturates, we compute the effective Z_{33}^* charge of each atom in PbTiO_3 under strains, by finite difference $Z^* = \frac{\Omega}{e} \frac{\Delta \mathbf{P}}{\Delta \mathbf{r}}$. Under zero strain, the effective charges (denoted as Z_0^*) are 3.65 (Pb), 5.76 (Ti), -4.90 (O1), and -2.28 (O2). With strain, we are interested in the change of the effective charges, namely $|Z^*| - |Z_0^*|$, given in Fig.2(c). Note that although the polarization increases once we turn on compressive strain, the effective charge nevertheless *decreases* for all atoms. In other words, the $|Z^*|$ has its maximum at the equilibrium structure. It is also interesting to recognize that the $|Z^*| - |Z_0^*|$ in Fig.2(c) separate into two groups: one group consists of Ti and O1 atoms, while the other is formed by Pb and O2 atoms. The strain dependence of the effective charge is very similar within the same group, implying the occurrence of a chemical correlation. Meanwhile, we note that the Z^* do not saturate—and

for instance, the Z^* of Pb (also of O2) slightly increases when the a length is below 3.7\AA . Since $\delta\chi_3 = \sum_i \{\delta Z_i^* \Delta r_{i,z} + Z_i^* \delta(\Delta r_{i,z})\}$ (where i is the index of atom), the saturation in χ_3 thus results from a balanced cancellation between strain-induced variations of Z^* and atomic displacements.

We now provide microscopic insight into why polarization undergoes a (puzzling) change from stage I to stage II, and why χ_3 saturates at high strains, by examining electron charge distributions (Fig.3). The electron distribution in equilibrium PbTiO_3 is as expected: charge transfer leads to electron deficiency near atomic cores (blue regions), while more charge accumulates in the interstitial area between atoms (red regions). As PT is strained to $a=3.80\text{\AA}$, an important change occurs, namely the overlapping charge largely disappears between Ti and O1 atoms. This reveals that the (considerably) weakened Ti-O1 bond is the reason responsible for the transition from stage I to stage II. It also explains why the c/a is enhanced in the second stage.

On the other hand, when PbTiO_3 is further strained to $a=3.72\text{\AA}$, electron charge near the O3 atomic core is *heavily* deformed, as a result of two factors that (1) more electrons are transferred into the interstitial between Ti and O3, and (2) the strong Coulomb repulsion from these interstitial charges distort the electrons near the O3 nuclei. In this circumstance, electrons between Ti and O3 behave more like strongly correlated particles. Further, since the electrons near the O3 nuclei couple directly with this ion, ionic displacement and electron deformation are thus expected to be correlated as well. This expectation is indeed confirmed by the electronic (P_{el}) and ionic (P_{ion}) contributions to the total (P_{tot}) polarization [Fig.2(d)]. When a decreases from a_0 to 3.72\AA , P_{el} rises faster than P_{ion} declines, giving rise to an overall enhancement of the total polarization. However, when a is below 3.72\AA , the P_{el} and P_{ion} contributions show equal slopes but with opposite signs (due to the above-described electron-ion correlation), thus leading to the polarization saturation in stage III. Another interesting indication of the strong electron-ion correlation is manifested by the *fine* structure on how the Ti-O3 bondlength depends on strain [see the inset of Fig.2(d)]. We find that when χ_3 starts to saturate near $a=3.72\text{\AA}$, the Ti-O3 bondlength surprisingly begins to *increase*. This demonstrates the existence of a minimum length (B_{min}) by which the Ti-O3 short bond can be compressed. Our predicted B_{min} is 1.76\AA (PT), 1.78\AA (BT), and 1.79\AA (ST). Reaching this minimum length implies the onset of polarization saturation.

In summary, density functional calculations on strained FEs reveal two unusual properties

of polarization: (1) the occurrence of stage II with distinct behaviors, and (2) the saturation of polarization upon higher strains. We further predict that the continuous transition from stage I to II may produce marked piezoelectric responses. Microscopic insights responsible for these behaviors are discussed. The enhanced piezo-response and c/a ratio in stage II is associated with the weakening of the Ti-O1 bonds. On the other hand, the electron-electron and electron/ion correlations lead to the polarization saturation. Our calculations reveal the existence of a profound limit up to which polarization can be enhanced by strain. The predicted saturation value of polarizations are larger than $125 \mu\text{C}/\text{cm}^2$ for three substances, suggesting that currently there is still room for polarization enhancement. This work was supported by the Office of Naval Research. We thank H. Krakauer and D. Vanderbilt for very useful discussions.

Note added: After having completed the manuscript, we were brought to a recent study[21] where the polarizations in highly strained $\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ films (with $c/a \approx 1.09$) is surprisingly similar to that in relaxed PZT films (with $c/a \approx 1.05$). This, in spirit, adds further evidence supporting the validity of our results on polarization saturation. Nevertheless, our key conclusions that (1) polarization saturates in all materials, thus being a universal principle; (2) the saturation origins from strong electron-ion correlation; (3) there is an unusual volume expansion and an enhanced c/a structural response between points A and B, have not been addressed previously[21].

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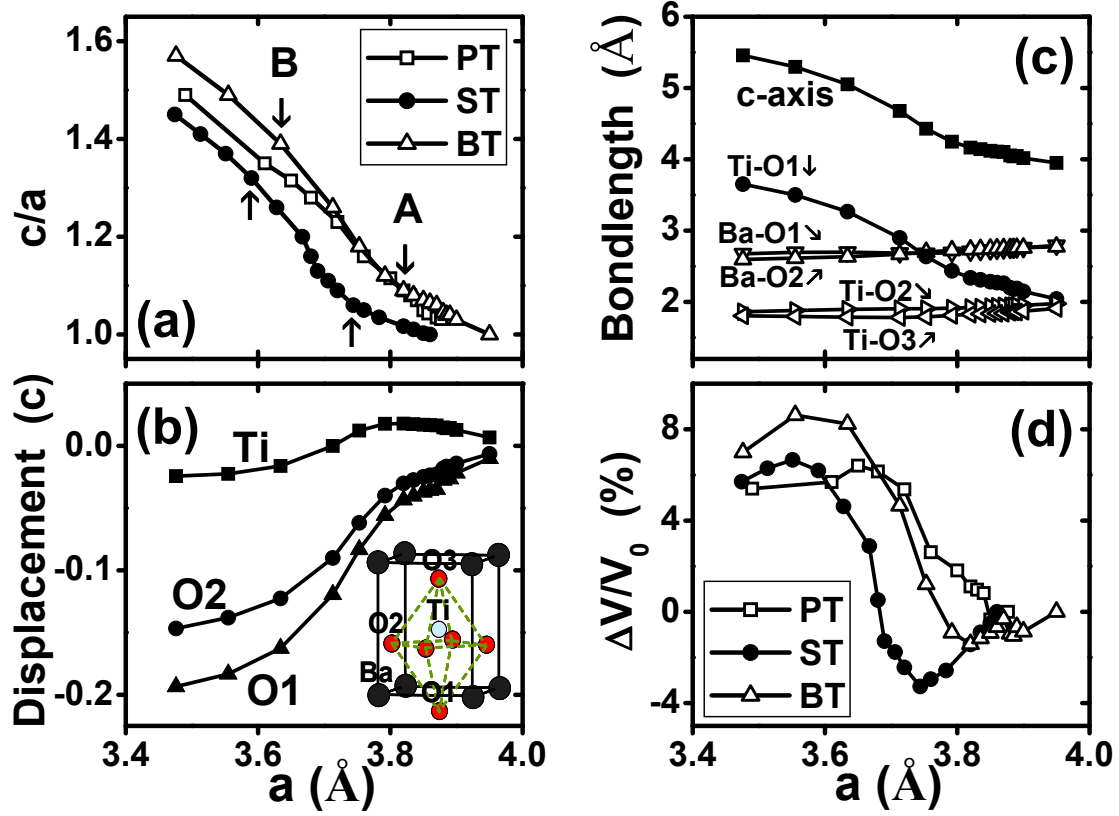


FIG. 1: Structural properties as a function of inplane lattice constant: (a) the c/a ratios (where points A and B are marked only for BT and ST, for the clarity of display), (b) atomic displacements in BaTiO_3 , (c) bond lengths in BaTiO_3 (where the c -axis length is also plotted for comparison), (d) the change of cell volume $\Delta V/V_0$ (where V_0 is the equilibrium volume). Labels of atoms in tetragonal perovskite are given in the inset of (b).

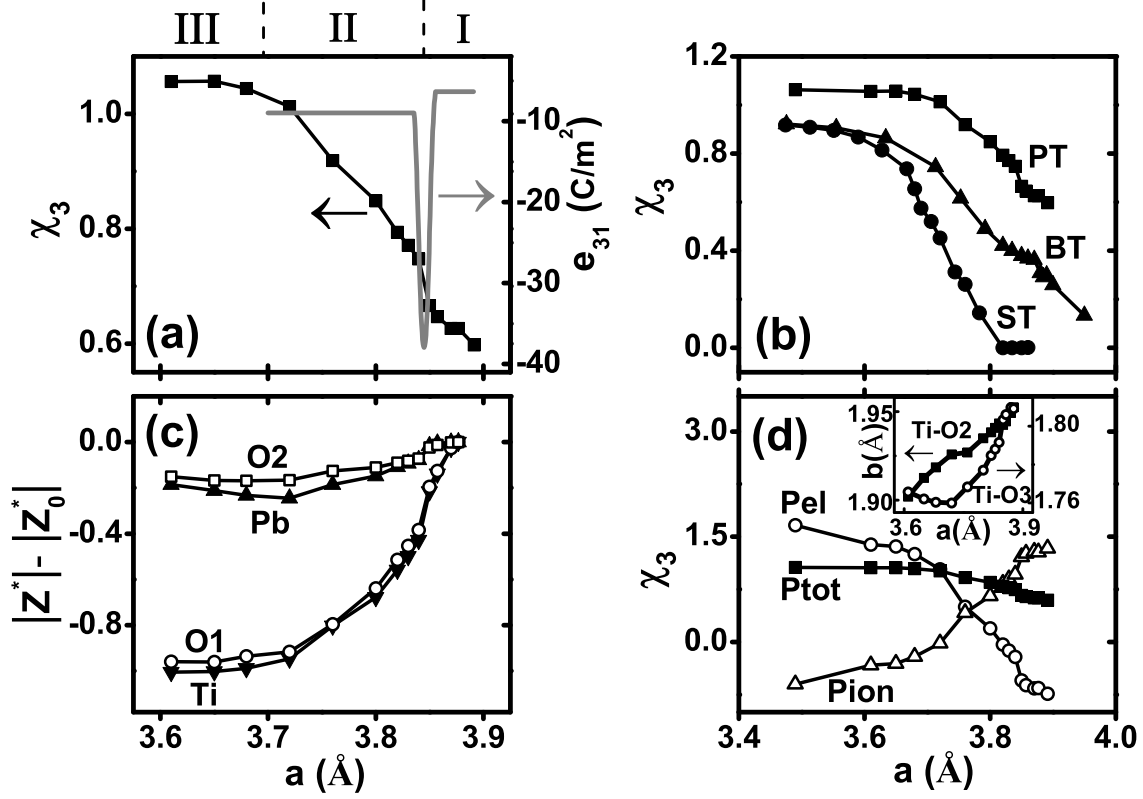


FIG. 2: Dependencies of the following properties as a function of the inplane lattice constant: (a) the χ_3 component of polarization (using the left vertical axis) and piezoelectric e_{31}^{pro} coefficient (using the right vertical axis) in PbTiO₃, (b) the χ_3 polarizations in BaTiO₃ and SrTiO₃, compared with that in PbTiO₃, (c) effective charges $|Z^*| - |Z_0^*|$ in PbTiO₃, and (d) electronic (P_{el}) and ionic (P_{ion}) contributions to the total (P_{tot}) polarization in PbTiO₃. For each calculated point in (d), the A-site atom is always placed at the cell origin so that comparison of P_{el} at different lattice constants are meaningful. Inset of (d) shows the fine structure of Ti-O2 and Ti-O3 bond lengths (b) versus the inplane (a) constant.

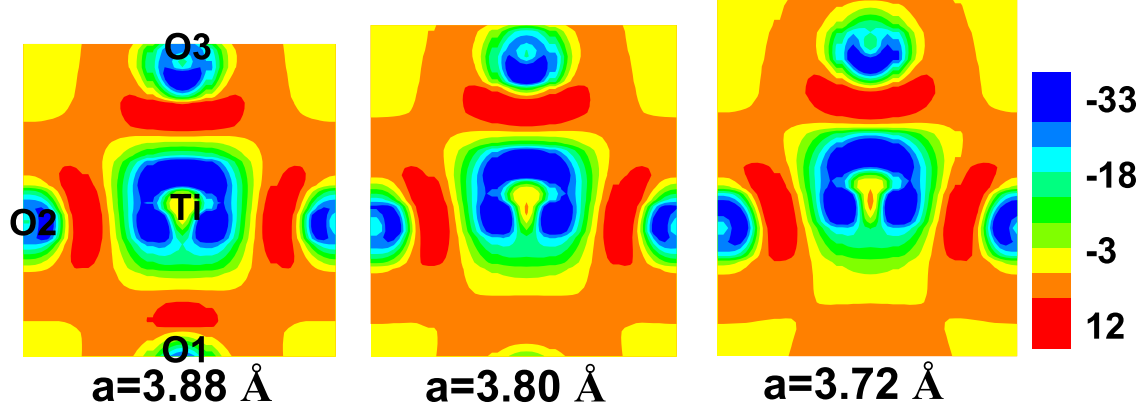


FIG. 3: (Color online) Charge-density difference $\Delta\rho = \rho - \rho_0$, where ρ_0 is the sum of electron density of free atoms, in PbTiO_3 at three different inplane lattice constants of $a=3.88$, 3.80 , and 3.72\AA . The plotted density is on the plane that cuts through the Ti, O1, O2, and O3 atoms.